

LA-UR-82-3557

CONF-820909--12

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LA-UR--82-3557


DEBB 004733

TITLE: Plutonium Roundtable Discussion

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SUBMITTED TO: Plutonium Chemistry  
(Proceedings of the 184th ACS Meeting, Kansas City, MO,  
September 15, 1982)

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Plutonium Roundtable Discussion  
184th ACS Meeting, Kansas City, MO, Sept. 15, 1982

R. A. Penneman - Chairman  
Los Alamos National Laboratory, University of California  
Los Alamos, New Mexico 87545

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Remarks by R. A. Penneman, Round Table Discussion Leader:

"This program on the 40th year of plutonium chemistry reminds us anew that plutonium has an exceedingly complicated chemistry. The near identity of its oxidation/reduction couples makes all oxidation states accessible and provides a wealth of chemistry not exceeded in any other element.

"Indeed, plutonium marks an important turning point along the actinide series of elements, both in its chemistry and in the metallic state. The metallic state of plutonium is the most complicated known. Metals beyond plutonium are abruptly simpler. Also, the chemistry changes dramatically for elements beyond plutonium. For plutonium, valences 3 - 7 are known, with oxidation states of 3 through 6 being common. For the elements americium and curium, just beyond plutonium, their tetravalent states are such powerful oxidants [ $\sim 1.5$  to 2 volts higher than that for Pu(IV)] that their tetravalent ions are essentially missing from aqueous chemistry. Without powerful oxidative intervention accompanied by complexation, this barrier of the tetravalent states beyond plutonium is not surpassed. This denies access to the pentavalent and hexavalent states of americium in ground waters, for example. In contrast, the higher valent states of plutonium can be prominent in aqueous solution, especially at ground water pH's frequently encountered.

"In this symposium we have heard papers describing process chemistry, new complexing extractants, pyrochemical processing methods, spectroscopy, and photochemistry. The groundwork for these approaches is of earlier origin just now being pursued, however elegantly. Further, we saw several papers on plutonium hydrolytic behavior, leaching and speciation at midrange pH's. A pattern seems obvious and indicates to me the consequences of diminished funding for investigations of basic plutonium chemistry and funding focused on certain problem areas.

"Where do we stand? Many needed complexity constants are unknown or poorly known. Questions of solubility under a variety of circumstances remain largely unanswered. Prof. Fuger summed

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up his presentation with the conclusion that plutonium thermochemistry is not in good overall shape. The field of organometallic chemistry is largely untouched. It is obvious that much remains to be done."

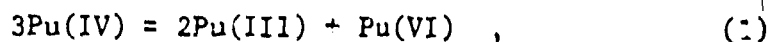
Speakers and audience members were encouraged to submit written versions of their participation. Edited versions follow.

There was considerable corridor discussion after a presentation by Dr. G. L. Silver, who "got the attention of the audience" by taking plutonium chemists to task concerning (according to him) their erroneous use of a (too) simplified summary equation involving the disproportionation of Pu(IV) and their lack of appreciation of alpha coefficients. Dr. Silver stressed the use of alpha coefficients and equations which explicitly involve acidity, hydrolysis of Pu(IV), and especially the presence of Pu(V), which is too frequently ignored.

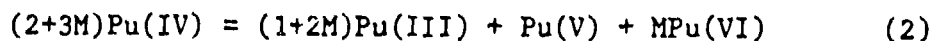
To illustrate the points of contention, accounts of Dr. Silver's arguments and a reply by Dr. Bell (edited and softened) are given.

Dr. G. L. Silver, Monsanto Research Corp., Mound, Miamisburg, OH 45342:

"In plutonium chemistry I find certain deficiencies which impede the orderly development of this science. One of these deficiencies is continued use of the equation:



which is supposed to represent the disproportionation of initially pure tetravalent plutonium. This equation is wrong for the purpose because it violates mass and charge conservation. I suggest the following equation as a replacement for Eq. (1):



in which M is the equilibrium ratio  $[\text{Pu(VI)}]/[\text{Pu(V)}]$ , and is found as the sole positive root of a cubic equation. This cubic equation contains coefficients which are functions of the acidity. The consequence is that Eq. (2) shows that both the extent of disproportionation and the stoichiometry of disproportionation are dependent upon the acidity, something lacking in Eq. (1). But having said this, I disavow Eq. (2) as inadequate for the general description of plutonium in solution. Both Eqs. (1) and (2) place too much emphasis on oxidation number  $N = 4.00$ . We need a method which explicitly defines the oxidation state distribution for any value of N, for any acidity, and for any degree of sequestration of the four oxidation states. These advantages are accomplished with the aforementioned cubic equation. It is found as Eq. (3) in *Radiochimica Acta* 21, 54 (1974) and is used with Eqs. (7)-(10) therein for determining fractional distributions of oxidation states for selected values of N ( $3 < N < 6$ ) and acidity.

Plutonium in solution is a function of six variables. The first two of these variables may be selected almost at pleasure. If plutonium oxidation number N and acidity are selected, the

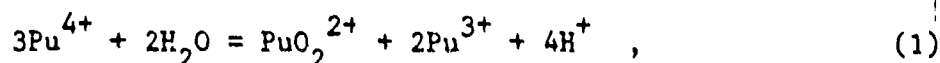
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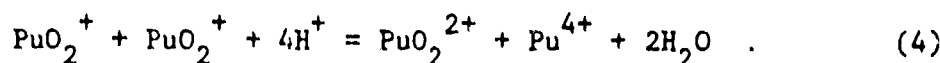
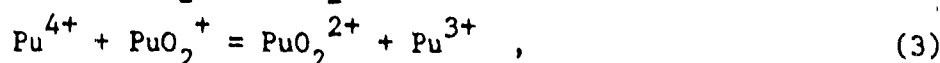
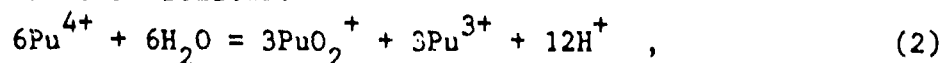
aforementioned cubic equation results. A calculator program and a commentary for this approach are given in MLM-2809 (1981). Specifying N restricts permissible oxidation state distributions in a way not generally appreciated. If measured system redox potential and acidity are selected, the system is even easier to solve. This approach is discussed in MLM-2727 (1980) and references cited therein, and will be illustrated again in the journal Marine Chemistry in 1983. Many other selections for the first two variables are possible. The latter four variables I take as the four alpha coefficients, one for each oxidation state of the plutonium. I choose alpha coefficients because they are easy to handle in the algebra of oxidation state distributions, and because their introduction suggests a new and potentially useful method of studying environmental plutonium. The alpha coefficient is the ratio of the total concentration of soluble oxidation state, including all complexes, to the concentration of the uncomplexed oxidation state."

Dr. J. T. Bell, Chem Tech Division, ORNL, Oak Ridge, TN 37830:

"A major thrust of Silver's comments was directed toward the reaction which is commonly and accurately called the disproportionation of Pu(IV). The reaction is frequently written as



and is generally understood to be the sum or "net reaction" of three reactions as follows:



Plutonium chemists use reaction (1) as the net reaction for reactions (2), (3), and (4). This is clearly documented in the Plutonium Handbook edited by Wick, and in Cleveland's book, The Chemistry of Plutonium. Reaction (1) is an accurate representation of an equilibrium and the equilibrium concentration quotient is the product of the quotients for reactions (2), (3), and (4). Therefore, it is correct to discuss equilibrium concentrations of Pu(IV), Pu(VI), and Pu(III), without Pu(V). Circumstances where the net reaction has not been properly considered are those where concentrations of oxidation states in solutions with low acidity are calculated without consideration of Pu(IV) hydrolysis and polymerization. The distributions of Pu oxidation states (including Pu(V) and Pu(IV) polymer in nitric acid systems) were reported in JINC 35, 609 (1973), and Silver has not included those experimental results in any comparison of experimental information with his computed results. The Pu(IV) hydrolysis and polymerization reactions have more effects on the oxidation states

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in reaction (1) at low acidities than any other reaction, and failure to consider the hydrolysis is negligence by choice.

Silver was critical of the lack of use by plutonium chemists of  $\alpha$ -coefficients. Assuming that Silver was referring to  $\alpha$ -coefficients defined as the fraction of the total concentration of a substance that exists as a particular species, he was wrong to say that plutonium chemists have not used them. Phil Horwitz at ANL has used them. Publications from ORNL have reported them to easily show relative concentrations of plutonium species, and L. M. Toth used such  $\alpha$ -coefficients as percent of Pu(IV) polymer in his symposium talk Tuesday. Alpha coefficients are a commonly used, simple concept - certainly since Ringbom's article in the Journal of Chemical Education in 1958."

Dr. Silver:

"Any one of Bell's Eqs. (2), (3), or (4) is a linear combination of the other two, and therefore it contributes no new information. The disproportionation can be represented by combining two such equations, but every value of the solution acidity has its own particular combination, usually not expressible with small integers, and no single combination is suitable for all acidities - see Radiochem. Radioanal. Letters 27 (4), 243 (1976)."

## REFERENCES TO REMARKS BY G. L. SILVER

1. Silver, G. L., "Method for Estimating Acidity Changes in Plutonium Solutions," Radiochimica Acta 1974, 21, 54.
2. Silver, G. L., "Comment on the Evaluation of the Chemical Forms of Plutonium in Seawater and Other Aqueous Solutions," to be published in Marine Chemistry (1983).
3. Silver, G. L., "Simplex Characterization of Equilibrium: Application to Plutonium," Radiochem. Radioanal. Lett. 1976, 27 (4), 243.
4. Silver, G. L., in "Mound Facility Activities in Chemical and Physical Research: July-December 1980" (April 10, 1981), MLM-2809, 50 pp.
5. Silver, G. L., in "Mound Facility Activities in Chemical and Physical Research: July-December 1979" (June 18, 1980), MLM-2727, 54 pp.

W. W. Schulz, Rockwell Hanford Operations, Energy Systems Group, P.O. Box 800, Richland, WA 99352:

"I am not going to comment on plutonium process chemistry or process R&E needs since I had done all that in my paper on Tuesday.

"I emphasized and seconded what Rai called out - namely the great need for experimental work to determine solubility data for plutonium in its various oxidation states under typical expected geologic repository conditions (e.g., pH, Eh, temperature, etc.).

"I mentioned that new computer codes - RAFSCATT 1 and RAFSCATT 2 have been very recently formulated by Dr. Gary Jacobs and Mr. William Anderson of Rockwell Hanford's Basalt Waste Isolation Project. These codes relate required engineered barrier (i.e., waste packages and seals performance to draft NRC and EPA criteria). A key part of these codes is that they partition

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radionuclides in those whose release are solubility-controlled (e.g. plutonium) and those whose release are not solubility-controlled (i.e., radiocesium). Reliable plutonium solubility data are thus a prerequisite to successful application of RAFSCATT 2.

"Regarding plutonium solubilities, judgment needs to be made upon how much time and money to spend determining exact Pu solubilities when all that may be required is to demonstrate that Pu solubilities are acceptably low for repository licensability purposes.

Phil Horwitz asked me to comment on what I saw as potential disadvantages of the various plutonium pyrochemical processes extolled by speakers in the Tuesday sessions. I, too, am a fan of pyrochemical techniques. I recognize that pyrochemical processes for Pu processing are just in their infancy - on batch plant-scale. To be truly useful, such processes need to be operated on a continuous basis. Scientists and engineers concerned with such technology need to develop equipment and procedures required to operate pyrochemical processes in a cost-effective, continuous manner."

Dana C. Christensen, Group MST-13, MS E511, Los Alamos National Laboratory, Los Alamos, NM 87545.

"A. The 'Twenty Year Retrieval Storage' has allowed us to continue operating while alternate methods of disposal could be established. The twenty year retrieval concept will become one of three things in the not too distant future.

1. Twenty Year Retrievable Interim sites will become permanent disposal sites. Or
2. The waste material will be exhumed and placed in permanent disposal sites. Or
3. The waste material will be exhumed and reprocessed. New waste criteria will be applied to the subsequent residues which will be compatible with the permanent disposal sites.

"The ultimate disposition of existing wastes is of major concern, particularly if they must go through additional processing in order to be handled in permanent disposal sites. The real concern is that we continue to generate wastes which must go through interim storage before they reach their grave. Most liquid wastes are reduced in volume by evaporation and blended with the solid material and cement to make a solid concrete matrix. This concrete is then sent to the twenty year retrievable storage site.

"At Los Alamos, we are making a concerted effort to reduce this waste volume to a minimum. In effect, we are trying to look beyond the need for permanent waste repositories by evaluating new processing and recycle concepts.

"B. A major effort is going into the pyrochemical processing area. Pyrochemical processing affords the luxury of working with high-density feeds and reagents thus requiring reduced floor space. The reagents are typically metal/salt couples which are essentially radiation resistant. Since we are working with plutonium in

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the high-density form (preferably molten metal), self attenuations reduce personnel exposures. The reagent salts have a high potential for recycle with little waste generation. We have demonstrated essentially every unit operation in a plutonium-recovery sequence with the exception of total-reagent recycle. Therefore, the near term requirement for the plutonium processing industry is to develop and demonstrate an integrated process sequence where the only wastes are those undesirable elements which entered with the plutonium feed. The emphasis should be to recycle all reagents.

"The longer term goal for pyrochemical processing is to convert the present batch systems to remotely operated hot cell environments. Pyrochemical processes typically involve reactions of chloride-based salts with plutonium at around 800°C. To date, designing systems with compatible materials of construction has been a great challenge. Two options exist in applying these systems to remote operations: 1) The hot cells must adapt to batch-type operations; or, 2) The batch systems must adapt to the conventional continuous/semicontinuous flow schemes of the present hot cells. The biggest engineering challenge will be to apply the fully integrated process sequence to remote facilities, with the emphasis on generating the smallest quantity of ultimate waste.

"The success of the entire nuclear industry in the United States rests almost exclusively on our ability to properly handle reprocessing wastes. Pyrochemical processes, as demonstrated in the plutonium industry, show great promise toward generating only a small volume of ultimate waste through high-yield processes and high (potential) reagent reuse. A concerted engineering effort, primarily in the process applications area, is needed to apply these new processing and recycle concepts to our processing facilities of the future."